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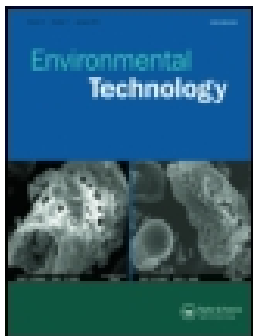
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Nutrients' distribution and their impact on Pangani River Basin's ecosystem – Tanzania

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ABSTRACT

Surface and groundwater from Pangani River Basin (PRB) were sampled in dry and wet seasons, analysed for dissolved organic and inorganic nutrients (N, P, Si and Urea). There was spatial and seasonal nutrients' variability, with enrichment of dissolved inorganic fractions accumulated from natural and anthropogenic sources. Silicates increased in dry season, whereas nitrate, ammonium, phosphate and urea increased in wet season; except for phosphate, other nutrients increased from upstream to the river mouth. High rate of chemical weathering possibly due to tropical climate and volcanic rocks has caused PRB to have higher concentration of silicates than average freshwater African Rivers. Contribution of PRB to the coast of Indian Ocean was 2.6, 39.0, 45.2, 67.4 and 5444.8 (mol/km²/yr) for nitrite, phosphate, ammonium, nitrate and silicates, respectively, which were lower than most of the tropical rivers in the world. Levels of nitrate and phosphate for most of the stations were higher than recommended levels for aquatic ecosystem health. Furthermore, observed hypoxia condition in some stations threatens aquatic life. This study recommends the efficient use of fertilizers to reduce nutrients' uptake into the lakes and rivers so as to meet the recommended level for aquatic and human health.

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Introduction

Structure and function of aquatic ecosystems are deteriorating rapidly in recent years due to human interactions [1,2]. Use of fossil fuels, food production and population growth have increased nutrients' (particularly nitrogen and phosphorus) loading to surface and ground water [3–5]. Global population growth is projected to reach 8 billion people by 2028 [6]; food demand will also increase. Most of the foods are expected to come from existing farmlands [7]; application of fertilizers can increase food production to feed the growing population but pose threat to the quality of surface and groundwater [4].

Nutrients are of paramount importance to aquatic ecosystem healthy, as primary producers need nutrients for growth and metabolism [8,9]. Biomass of primary producers decreases when concentration of nutrients is below optimum amount needed to support their growth. However, excessive nutrients lead to poor water quality, resulting in loss of biodiversity, eutrophication, decreasing dissolved oxygen (DO) and ultimately death of aquatic organisms [10].

Ecosystem good health is an essential condition for an ecosystem to deliver, regulate, provide and support

ecosystem services to human beings [11]. Supply of those services will decrease if the ecosystem is unhealthy, and ecosystem health will continue to degrade unless restoration measures are taken [2,12]. Most of human dominated aquatic ecosystems have become dysfunctional and high nutrient content is one of the causes [13].

Land-use changes have increased significantly in many of African river basins owing to rapid development, urbanization, industrial activities and intensification in agricultural activities [5,14]. These changes have been associated with increasing nutrients in most of African rivers, thus calling for the need of monitoring and introducing strategies for management of nutrient levels. This becomes an important agenda from the fact that many places in Africa especially in rural areas people use water from the river without any treatment [15]; therefore, increasing nutrients in water can have impacts not only to aquatic ecosystem but also to human health.

Pangani River Basin (PRB) is among the largest and most important basin in north-eastern part of Tanzania [16], for goods and services, including hydroelectric power, drinking water, laundry, fishing, fuel wood and

agriculture. Population increase, land-use change and pollution from agricultural sources have increased the challenges to PRB's ecosystem health [17]. Population survey of 2012 showed that regions of Kilimanjaro, Manyara, Arusha and Tanga had 6.8 million people who in one way or another depend on resources from PRB for their livelihood. With a growth rate of 1.6%, 3.2%, 2.7% and 2.2% for Kilimanjaro, Manyara, Arusha and Tanga, respectively, the basin will have more than 10 million people in the coming three years, which will increase pressure for food and other services from the basin [18].

Agriculture is one of the major economic activities in PRB. It goes hand in hand with application of fertilizers; according to Elisante and Muzuka [19], application of fertilizers in Tanzania has increased from 0.12×10^6 metric tonnes in 2005/06 to 0.263×10^6 metric tonnes in 2009/10. Similarly, the use of fertilizers in PRB is increasing with time [17]. The current emphasis of the government to improve agricultural output popularly known as 'Kilimo Kwanza' (means agriculture is the first priority) is likely to increase the use of organic and inorganic fertilizers, which will likely increase the levels of nutrients in the PRB. Furthermore, previous studies have also shown that nutrient levels in PRB have been increasing with time [20].

However, most of the previous studies addressed mainly water quality for human consumption and disregarded ecosystem health; phase partitioning between organic and inorganic nutrients, and chemistry of dissolved silicates (DSi) were not studied. The PRB discharges to the South-West Indian Ocean (SWIO), but unfortunately no research has estimated contribution of nutrients from PRB to the coast of the Indian Ocean. In the water resources management level, there was insufficient knowledge on the current nutrients status covering the entire basin. Therefore, the missing information represents significant gap to better understanding nutrient content, yield and chemistry of PRB. The study was therefore undertaken with the following objectives: (i) to ascertain the spatial and seasonal nutrients variability, their sources and possible effect to PRB aquatic ecosystem and human health; (ii) to estimate contribution of nutrients from PRB to the coast of SWIO and thereafter, compare with rivers from SWIO and other rivers around the world. The study also provides the current status of nutrients covering the entire basin, which will help the basin management officers to carryout water resources management measures based on the current status.

The study hypothesized that there was significant spatial and temporal nutrients' variability and the levels of nutrients were above the recommended levels, thus posing significant threat to impact human and aquatic ecosystem health.

Material and methods

Study area

Pangani River Basin is the third largest in Tanzania ($43,650 \text{ km}^2$) [20] after Rufiji basin ($177,000 \text{ km}^2$) [21] and Ruvuma ($53,330 \text{ km}^2$) [22]. About 95% of the basin is found in Tanzania with the remaining 5% is located in Kenya. The basin is located between latitudes $3^\circ 03'S$ and $5^\circ 59'S$, and longitudes $36^\circ 23'E$ and $39^\circ 13'E$, occupying parts of Kilimanjaro, Manyara, Arusha and Tanga regions (Figure 1). The Kilimanjaro and Meru mountains are considered as major sources of water to the river [24], with various streams originating from these mountains flowing downward joining one another before draining into Nyumba ya Mungu Reservoir (NYR). The Reservoir covers an area of about 150 km^2 [17], constructed in 1965 for water supply, irrigation, flood control and hydroelectric power production [16]. Thereafter, the main Pangani River flows from the reservoir to the Indian Ocean; on its way receives additional water from Mkomazi, Soni, Mkalamo and Luengera tributaries.

The basin has bimodal type of climate due to the north and south movement of inter-tropical convergence zone. Short rainy occurs from October/November to December while long rainy occurs from March to May, and dry season occurs from July to October [20]. In general, rainfall increases with elevation; mountainous ranges of Kilimanjaro, Meru, Pare and Usambara are located in the north and eastern part of the basin (with elevation $>2200 \text{ m}$), which, together with the coastal areas, receive a high rainfall ranging from 650 to 3150 mm per year. Central and western parts have semi-arid to arid climate, with rainfall ranging from 350 to 650 mm per year [24]. On the other hand, a large part of the basin experiences high temperature throughout the year with the maximum temperature ranging from 32°C to 35°C in January–February, while the minimum temperature ranging from 14°C to 18°C in July–August [25]. Opposite to the rainfall, the temperature decreases with height giving a lapse rate, ranging from 0.51°C to 0.56°C per 100 m rise [26].

Sampling and analytical methods

Water samples from 39 stations, including rivers, lakes and ground-wells (Table 1), were sampled in dry season (October 2014) and wet season (May–June, 2015). Acid-cleaned 1 L polyethylene bottles were used to collect surface and groundwater. Water samples were filtered by $0.45 \mu\text{M}$ pore size cellulose acetate filters pre-cleaned by double-distilled hydrochloric acid (HCl) at $\text{pH} \leq 2$, then washed with Milli-Q water.



Figure 1. The study area, with sampled stations represented by similar numbers as Table 1, geographical regions making the basin, elevation in different areas. Mt. KLM and Mt. Meru are the abbreviation for Mount Kilimanjaro and Meru, respectively. Modified from [23].

Saturated mercury chloride solution was used to preserve filtered samples and kept in pre-cleaned 60 ml HDPE Nalgene bottles. After sampling, preserved samples were packed in cool ice box and transported to State Key Laboratory of Estuarine and Coastal Research (SKLEC) in the East China Normal University (ECNU) for chemical analysis. On-site measurement of temperature, pH, electric conductivity, DO and salinity was done by multi-parameter probe (Multi 350i Set 5 from Germany). The pH and DO meters were calibrated before measurement, where buffer solutions of pH 4.01 and pH 7.00 were used to calibrate pH meter. Water-saturated air calibration method was used to calibrate the DO meter after rinsing DO meter thoroughly with deionized water. Quality of the data was tested by triplicate measurement of samples, whereby standard deviation was $<10\%$.

Skalar SANplus Continuous Flow Auto-analyzer was used to measure nitrite, nitrate, ammonium, silicates,

phosphate, total dissolved nitrogen (TDN) and total dissolved phosphorus. The quality of nutrients' analyzer was checked by repeating analysis of some samples and the results showed the standard deviation of <5%. For TDN and TDP, alkaline potassium persulfate was used to digest samples at 120°C for 30 min and thereafter, the content of dissolved organic nitrogen (DON) was calculated from the difference between TDN and dissolved inorganic nitrogen (DIN) [27]. For urea as part of organic nitrogen compound, a UV-VIS spectrophotometer at 520 nm wave length was used to determine urea by a method described in [28]. The concentration of dissolved organic phosphorus (DOP) was also calculated from the difference between TDP and dissolved inorganic phosphorus (DIP, or PO_4^{3-}).

SPSS 16 was used for statistical analysis, and One-way ANOVA at 95% ($P \leq .05$) and 99% ($P \leq .01$) confidence intervals were used to determine significant levels of spatial and seasonal variations of different parameters.

Table 1. Stations name, and geographic location, number represented on map and elevation of the station (m) above mean-sea level.

River name	Lat (°S)	Lon (°E)	Number	Elevation (m)
Pangani River @ Mseko	5.40958	38.86875	1	6
Pangani River @ Mnyuzi	5.23361	38.56018	2	293
Luengera River @ the bridge	5.13515	38.50959	3	296
Pangani River @ Korogwe	5.16615	38.47371	4	287
Pangani River @ Mkalamo	4.98639	38.11254	5	489
Pangani River @ Buiko	4.64937	38.04159	6	533
Pangani River @ Naururu	4.18012	37.50136	7	639
Pangani River D/S Nyumba ya Mungu Dam	3.84022	37.46001	8	665
Soni River @ Soni	4.84554	38.36876	9	1179
Mkomazi River @ Bendera	4.60216	38.06852	10	470
Nyumba ya Mungu Dam	3.8128	37.45856	11	694
Lake Jipe @ Makuyuni	3.57702	37.73659	12	718
Lake Chala @ Safari lodge	3.30827	37.68885	13	847
Ruvu River @ Tingatinga	3.55712	37.48665	14	695
Ruvu River @ Kifaru	3.52601	37.56544	15	701
kikuletwa River @ TPC	3.51039	37.30484	16	712
Karanga River @ TPC	3.44025	37.30453	17	746
Chemka spring	3.44418	37.19363	18	845
Miwaleni spring	3.43086	37.44586	19	723
Miwaleni Borehole	3.43086	37.44586	20	721
chekereni/weruweru spring	3.35182	37.31507	21	872
Nsere springs	3.29528	37.25655	22	1023
Mwenge borehole	3.21793	37.32146	23	1039
Himo River @ the bridge	3.39046	37.54489	24	841
Karanga River @ the bridge	3.34118	37.31783	25	888
Weruweru River @ the bridge	3.3244	37.2589	26	957
Kikafu River @ the bridge	3.32416	37.21686	27	976
Marawee stream @ Marangu	3.24098	37.52092	28	1845
Sungu River @ Singandoo	3.21793	37.32334	29	1542
Mweka stream @ Mweka gate	3.21967	37.34151	30	1643
Machame stream @ Machame gate	3.17448	37.2396	31	1789
Maji ya Chai River	3.37073	36.8969	34	1224
Kikuletwa River @ Karangai	3.44816	36.85841	35	1020
Kikuletwa @ kambu ya Chokaa	3.45762	37.18767	32	842
kikuletwa @ power station	3.45488	37.21064	33	834
Them River @ Lokii mnadani	3.50879	36.78243	36	1029
Nduruma River @ NM-AIST road	3.40522	36.78165	37	1206
Nduruma River @ the bridge	3.37569	36.75114	38	1340
Them River @ Olesha Olgilai	3.33858	36.72075	39	1569

Pearson correlation coefficient was used to test significant correlation among variables. The change was considered as statistically significant at $p \leq .05$ or $p \leq .01$.

Results

Data were displayed in Table 2, giving their mean and standard deviation.

Pangani River Basin discharge to the Indian Ocean

River discharge data were taken from Pangani Basin Water Board (PBWB), which was measured at Mseko

Table 2. Concentration of nutrients and physicochemical parameters from PRB in dry and wet seasons (mean \pm SD) in μM , compared with previous study [20] and other rivers.

River	Country	Urea (μM)	SiO_3^{2-} (μM)	NO_2^- (μM)	NH_4^+ (μM)	NO_3^- (μM)	PO_4^{3-} (μM)	DOP (μM)	DON (μM)	Temperature ($^\circ\text{C}$)	pH	Dissolve oxygen (mg/L)	Ref.
PRB(dry)	Tanzania	1.19 \pm 0.40	702.71 \pm 318.15	0.33 \pm 0.23	4.08 \pm 2.86	34.7 \pm 37.72	1.98 \pm 1.76	1.14 \pm 0.91	15.52 \pm 10.95	23.66 \pm 3.77	7.83 \pm 0.91	6.19 \pm 2.51	This study
PRB (wet)	Tanzania	1.27 \pm 0.75	621.17 \pm 326.72	0.24 \pm 0.29	5.01 \pm 14.95	50.41 \pm 69.04	2 \pm 1.84	0.12 \pm 0.14	8.06 \pm 12.38	21.08 \pm 3.43	7.86 \pm 0.64	6.54 \pm 1.99	This study
PRB	Tanzania			38.69	9.46	1113	2.69						[20]
Sabaki	Kenya				0.5		4.27						[29]
Komati	Swaziland				28.57	43.57	24.52						[30]
Thukela	South Africa			145.78	80.25	12.98	21.25						[31]
Caura	Venezuela				2.5	4.64	0.08						[32]
Ishikari	Japan		323.93	0.714	12.14	66.43	0.97						[33]
Tapti	India		271.18			35.9	3.65						[34]
Trinity	USA		82			39.2	1.85						[8]
Narmada	India		192.6			31.92	1.84						[34]
Tana*	Kenya		338.16		0.59	20.08	1.49						[35]

(station 1) in the river mouth (Figure 1). This was the best station to represent variation of discharge for the entire basin. Among the five-years (2011–2015) acquired discharge data, 2015 had the highest discharge, while 2011 had the lowest discharge. Monthly average showed one principal peak in May, secondary peak occurred in February with the maximum standard deviation, while September had the minimum discharge (Figure 2). PRB is a small tropic river; its discharge fluctuates based on rainfall and drought event along the basin. Maximum and minimum discharge correspond to long rainy and dry season, respectively; the highest discharge ($33.2 \text{ m}^3/\text{s}$) being four times higher than minimum discharge ($8.80 \text{ m}^3/\text{s}$) reflects substantial input of water in long rainy season. Large standard deviation signifies discharge in PRB had strong inter-annual variability, caused by tropical climate where rainfall frequency and intensity were very variable [23]. Furthermore, there was a lag between onset of the short rainy season and rise in the water level. It seems that, the minimum pick occurred in February, whereas short rainy season always occurred between October and January.

Spatial and temporal variability of physicochemical water parameters

Water temperature is an important parameter for aquatic ecosystem affecting rate of chemical reaction, solubility

of gases and primary productivity. Water temperature in PRB ranged from 15.8°C to 30.2°C with an average of 23.7°C in dry season and 15.0°C – 27.7°C with an average 21.1°C in wet season reflecting that temperature was high in dry season compared to wet season (Table 2). Between rivers, lakes and groundwater, the average temperature was high in lakes 27.8°C in dry season and low temperature observed in rivers 20.6°C in wet season. Mean temperature for groundwater samples was 22.6°C almost the same in both seasons. In general, water temperature follows surrounding air temperature. Most of the tropical areas' high temperature occurs in the dry season due to clear sky increasing heat from solar radiation, whereas low temperature occurs in the wet season because of cloudy decreasing heat from solar radiation [36,37]. In addition to that, low water temperature in wet season was also contributed by cooling effects of rain water. Small difference between wet and dry season shows one of the characteristics of tropical climate where temperature difference between the two seasons are relatively low compared to other climatic regions. The lowest temperature of 15.0°C was recorded at Marawee stream in Marangu (station 28) located on slope of Mt. Kilimanjaro, while the highest temperature was recorded at Lake Jipe (station 12). This proves that temperature increased with a decrease in elevation supported by significant negative correlation between temperature and elevation ($r = -0.783$, $p \leq 0.01$). High temperature in Lake Jipe was

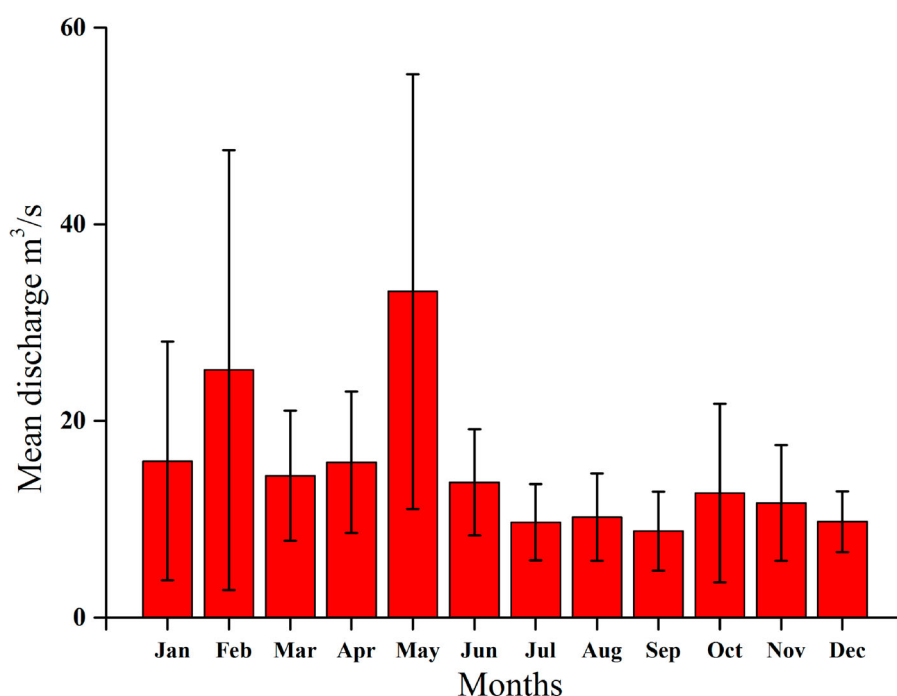


Figure 2. Histogram illustrating discharge of PRB at Maseko station; mean monthly discharge was calculated from daily discharge data accumulated for five-years data (2011–2015).

also caused by its location in semi-arid region and leeward side of north Pare Mountains.

Water pH explains acidic or basic nature of water; the pH of water can change due to biological activities and input of pollutants [37]. The pH value varied from acidic to alkaline (5.56–9.21) with an average 7.83 in the dry season and 5.21–8.79 with an average 7.47 in wet season (Table 2). Lakes had the highest mean pH of 9.01, whereas groundwater had the lowest pH of 6.70. There was significant positive correlation between temperature and pH ($r = 0.633$, $p \leq 0.01$), reflecting higher pH in dry season than in wet season (Table 3). The lowest pH was recorded at Marawee stream in Marangu (station 28) and the highest pH was measured at Lake Jipe (station 12). Optimum pH to most organisms is 6.5–8.5; deviating from this range can stress most of the aquatic organisms [38]. Most of the stations in PRB were within optimum range except Lake Jipe (pH = 9.3).

DO, which is an important parameter to support aquatic ecosystem, ranged from 1.01 to 9.1 mg/L with an average of 6.19 mg/L in dry and 1.09–9.97 mg/L with an average of 6.54 mg/L in wet season. The lowest DO was found at Lake Jipe, while the highest DO was measured at the Karanga River in TPC (station 17) (Table 2). Among rivers, groundwater and lakes, mean DO was low in lakes (5.64 mg/L), whereas high DO was measured in rivers (7.97 mg/L). Significant negative correlation between DO and temperature ($r = -0.461$, $p \leq 0.01$) reflects the increase of DO in wet season (Table 3). Most of the stations had conducive DO (≥ 5 mg/L) to support aquatic ecosystem except Lake Jipe (1.5 mg/L) and Ruvu River at Kifaru (1.76 mg/L). Lake Jipe collects runoff from neighbouring areas with intensive farming of coffee, maize and beans. Furthermore, decayed materials and papyrus reeds covered a large part of the lake, which ensure that the lake had high quantity of organic matter, whose decomposition increases oxygen depletion and led to hypoxia [39]. Ruvu River with hypoxia is the outlet from Lake Jipe.

Spatial and temporal nutrients' variability

Trend of nutrients' concentration in most of the stations were nitrite < urea < phosphate < ammonium < nitrate < silicates (Table 2).

The dissolved silicate (DSi) was the dominant inorganic nutrient in the basin, which occupied more than 90% of dissolved inorganic nutrients in both seasons. Concentration of DSi ranged from 99.2 to 1456 μM (average: 702.7 μM) in dry season and 175.3–1652 μM (average 621.7 μM) in wet season; large standard deviation of 318 and 327 in dry and wet season respectively reflect large spatial variability. Mean content of DSi in lakes, groundwater and rivers were 1117.1, 954.5 and 498.6 μM in wet season, while in dry season was 867.3, 980.8 and 633.7 μM , respectively. The results reflect that mean concentration of DSi was almost the same in groundwater in both seasons compared to that in lakes and rivers. There was a significant positive correlation between DSi and temperature ($r = 0.385$, $p \leq 0.01$), supporting the increase of DSi in dry season compared to wet season (Table 2). The lowest DSi was measured at Them River in Lokii mnadani (station 36), while the highest amount was recorded at Lake Jipe (station 12). Since most of DSi comes from weathering [40]; high temperature in Lake Jipe caused a high rate of weathering, leading to a high level of DSi in the lake. There was a significant negative correlation between DSi and DO ($r = -0.330$, $p \leq 0.01$) (Table 3), and a good example can be seen in Lake Jipe with highest DSi together with lowest DO. Another factor regulates weathering of DSi is geology of the rock; rate of weathering is higher in young rock than old one [40]. Upstream of PRB has young volcanic rock, which led to a high content of DSi relative to downstream rich in Proterozoic rock [41].

Ammonium ranged from 1.26 to 18.5 μM (average: 4.08 μM) in dry season and 0.62–91.6 μM (average 5.01 μM) in wet season. Seasonal change showed that average content of ammonium was higher in wet

Table 3. Pearson's two-tailed correlation table of different parameters.

	DSi	NH ₄ ⁺	NO ₃ ⁻	PO ₄ ³⁻	DOP	DON	Urea	Temp	Salinity	DO	Elevation
DSi											
NH ₄ ⁺	0.38*										
NO ₃ ⁻	0.34*	-0.18									
PO ₄ ³⁻	0.19	-0.22	0.36*								
DOP	0.16	-0.13	0.67**	0.17							
DON	0.42**	0.51**	0.29	0.29	0.08						
Urea	0.18	0.27	0.10	0.50**	-0.06	0.58**					
Temp	0.45**	0.29	-0.16	-0.04	-0.53**	0.34*	0.16				
Salinity	0.38*	0.37*	-0.21	0.04	-0.60**	0.48**	0.29	0.74**			
DO	-0.25	-0.43**	0.28	-0.16	0.41*	-0.30	-0.34*	-0.38*	-0.49**		
Elevation	-0.10	-0.13	0.26	-0.16	0.42**	-0.28	-0.23	-0.75**	-0.47**	0.38*	

Note: Bold numbers show there is correlation among the parameters.

*Significant at the $p \leq 0.05$.

**Significant at the $p \leq 0.01$.

season than in dry season (Table 2). The lowest content of ammonium was measured at Nduruma River (station 37), while the highest level was measured at Lake Jipe (station 12). Mean content of ammonium in lakes, rivers and groundwater were 2.63, 3.27 and 2.38 μM in dry season, while 47.1, 3.06 and 2.31 μM in wet season, respectively. The highest content in lakes was caused by a high amount of ammonium measured in Lake Jipe. Ammonium is a product of animal excretion, sewage, fertilizers and remineralisation of organic matter [42]. Decayed organic matters in Lake Jipe together with runoff from agricultural and domestic wastes were among of the sources of elevated level of ammonium in Lake Jipe. Furthermore, low level of DO in the lake, possibly hindered transformation of ammonium to nitrate.

Nitrite ranged between 0.16 and 1.03 μM (average 0.33 μM) in dry season and 0.16–1.82 μM (average 0.24 μM) in wet season. Seasonal change has showed that content of nitrite was higher in dry season than wet season (Table 2). The lowest concentration of nitrite was recorded at Himo River (station 24), while the highest amount was measured at Themí River in Lokii mnadani (station 36). Mean contents of nitrite in lakes, rivers and groundwater were 0.48, 0.34 and 0.16 μM in dry season, while in wet season were 0.13, 0.22 and 0.1 μM , respectively.

Nitrate ranged between 1.01 and 150.5 μM (average 34.7 μM) in dry season and 1.40–390.0 μM (average 50.4 μM) in wet season (Table 2). The lowest content of nitrate was measured at the outlet of Nyumba ya Mungu reservoir (station 8), while the highest amount was recorded at Themí River in Lokii mnadani (station 36). There was a large spatial variation of nitrate content within the basin (see a large value of standard deviation). Nitrate was the dominant DIN occupied 89% in dry season and 91% in wet season of the total DIN. On average, a high content of nitrate was measured in groundwater (110.27 μM) compared to 41.78 μM in rivers and 14.76 μM in lakes.

Phosphate ranged between 0.08 and 9.05 μM (average 1.98 μM) in dry season and 0.08–7.10 μM (average 2.00 μM) in wet season (Table 2). The lowest amount of phosphate was recorded at Soni River (station 9), while the highest content was recorded at Maji ya Chai River (station 34). Arusha was among of the region with low rate of fertilizers use applying 38% of cultivated lands compared to Tanga, Kilimanjaro and Manyara. Nevertheless, Arumeru district where Maji ya Chai and Themí River are located was leading with high use of inorganic fertilizers compared to other districts in Arusha [43]. Therefore, elevated phosphate and

nitrate in mentioned stations possibly were the outcome of fertilizer use. Furthermore, there was a significant positive correlation between phosphate and nitrate ($r = 375$, $p = .01$), signifying that they were coming from the same source. Averaging phosphate in groundwater, rivers and lakes revealed that the highest content of phosphate was observed in groundwater (3.02 μM), while lakes had the lowest amount (0.72 μM).

The concentration of nitrate in groundwater ranged between 0.06 and 279.8 μM , whereas phosphate was between 1.00 and 6.50 μM ; these amounts were higher than pristine river such as Caura River from undisturbed tropical forest [32]. Dissolved nutrients from different sources percolate into the soil during rainy season and come out as spring/boreholes water. Therefore, elevated levels of nutrients in groundwater samples in PRB signify that nutrients in this basin were not only from natural sources.

Average concentration of phosphate and ammonium in this study was in the same order of magnitude as measured in the previous study [20], but concentration of nitrate and nitrite was lower than reported in [20]. High nitrate and nitrite might be caused by coverage, since the previous study sampled few stations about 12 stations compared to 39 stations from this study. Besides, the previous study focused the main river and disregarded tributaries and groundwater.

The concentration of urea ranged between 0.51 and 2.44 μM (average 1.19 μM) in dry season and between 0.39 and 3.45 μM (average 1.27 μM) in wet season (Table 2). The lowest amount of urea was measured at Karanga River (station 25), while the highest amount was measured at Ruvu River in Tingatinga (station 14). Mean content of urea in groundwater and rivers was almost the same 0.99 and 1.27 μM , respectively compared to 1.53 μM measured in lakes. Being part of DON, its percentage (urea/DON) doubled from 8% in dry season to 16% in wet season. Urea is an important nitrogen source for aquatic micro-organisms released to freshwater from both natural and anthropogenic sources, such as fertilizers, herbicides, pesticides, and excretion of mammals and other animals [44]. Low content of urea in PRB was either due to low use of urea as fertilizers or urea was transformed into other form [45].

DON ranged from 0.40 to 44.8 μM (average 15.5 μM) in dry season and from 0.06 to 59.3 μM (average 8.06 μM) in wet season (Table 2). On the other hand, content of dissolved organic phosphorus (DOP) was lower than DON ranged from 0.17 to 2.63 μM (average 1.14 μM) in dry season and 0.01–0.69 μM (average 0.12 μM) in wet season (Figure 3). Both DON and DOP

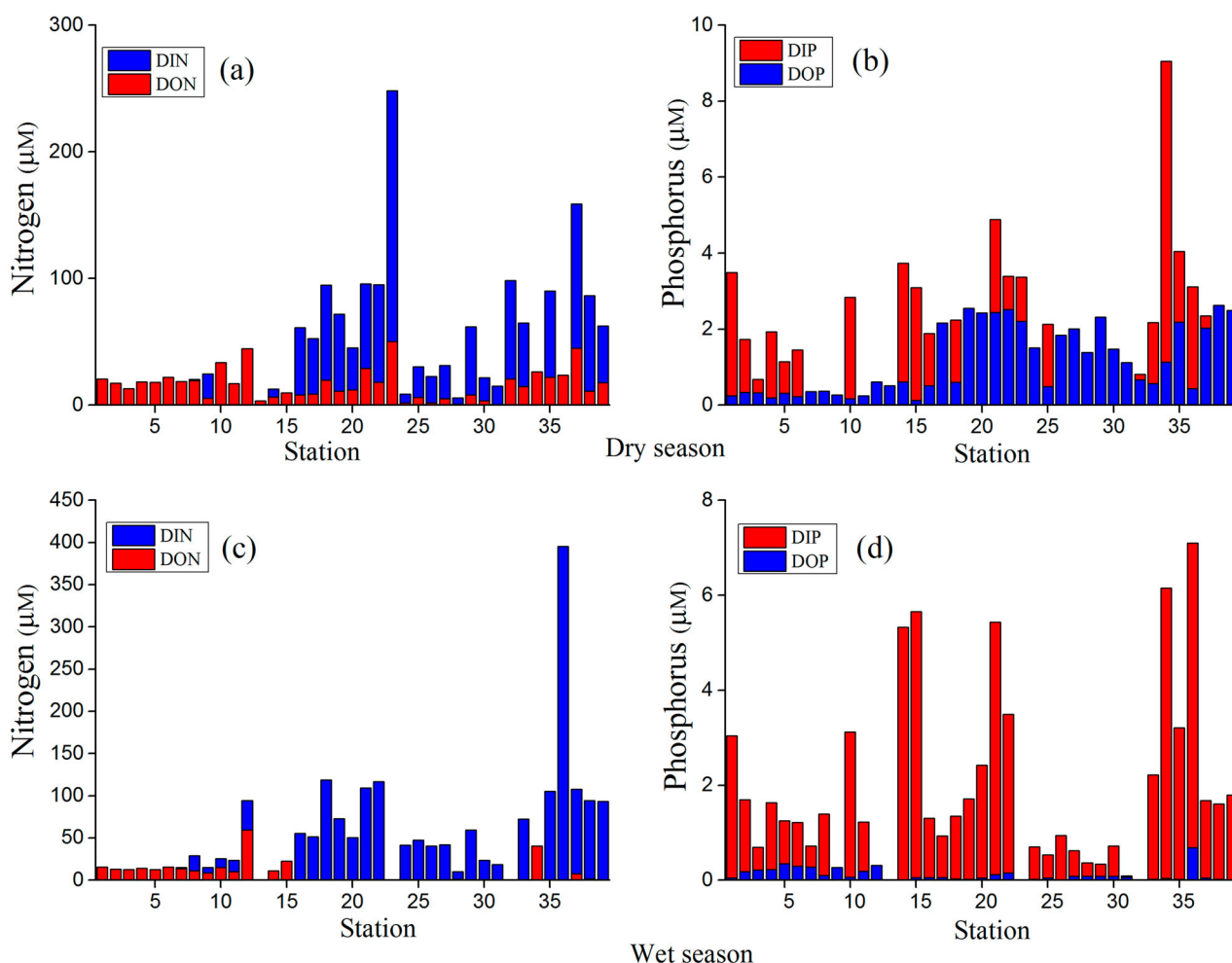


Figure 3. Spatial and seasonal organic and inorganic nutrients' variability.

increased in dry season compared to that in wet season. Averaging organic fraction in lakes, groundwater and rivers showed a high content of DON (28.16 µM) in lakes compared to 11.76 and 11.37 µM in groundwater and rivers, respectively. Mean DOP was 0.14, 1.1 and 0.5 µM for lakes, groundwater and rivers, respectively. Comparison between organic and inorganic fraction showed that in both seasons DIN was higher than DON (Figure 3(a, c)). Similarly, ratio of DIN/TDN increased from 0.74 in dry season to 0.88 in wet season, while DON/TDN decreased from 0.26 to 0.12, respectively. Dissolved inorganic phosphorus (DIP) was also a dominant fraction of phosphorus in dry and wet seasons relative to dissolved organic phosphorus (Figure 3(b, d)). DIP/TDP increased from 0.63 in dry season to 0.94 in wet season, while DOP/TDP decreased from 0.37 in dry season to 0.06 in wet season.

The composition of organic and inorganic nutrients in PRB was different from rivers drain pristine system with low atmospheric deposition. Natural unpolluted rivers

usually have low nutrients, dominated by DON and DOP [46]. In both seasons, DIN and DIP were the dominant species of dissolved nitrogen and phosphorus in PRB, justifying that there was a higher contribution of nutrients from inorganic sources than from organic ones. Therefore, a high concentration of DIN and DIP relative to DON and DOP also suggest that PRB was one of the rivers influenced by human activities [20, 47]; possibly wastes from agriculture, urbanization and industrial activities were cause of concern.

Concentration of nutrients getting into Nyumba Ya Mungu reservoir (NYR) composed of input from Meru and Kilimanjaro tributaries. Since there were two tributaries draining NYR, nutrients' inflow was calculated by summing up mean annual flux at Ruvu River in Tingatinga (station 14) and Kikuletwa River at TPC (station 16), while nutrient outflow was nutrients flux at Pangani River downstream in Nyumba ya Mungu reservoir (station 8) (Figure 1). In both seasons, concentration of nutrients getting into the reservoir was higher than

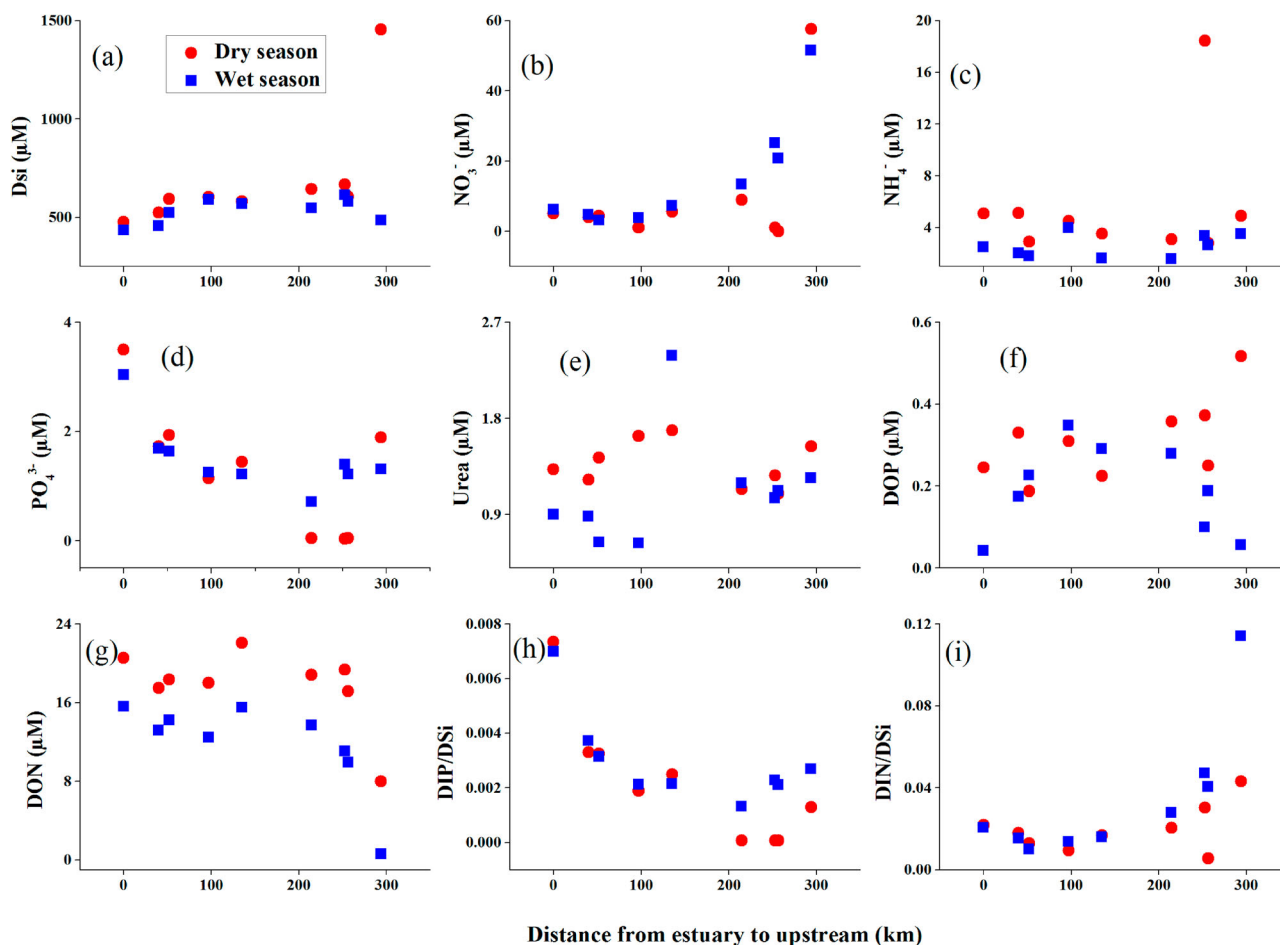


Figure 4. Nutrients' variability of the main river from the estuary to upstream the distance was estimated by Google Earth.

outflow from the reservoir (Figure 4). Mean annual flux of nitrite, phosphate, ammonium, nitrate and silicate getting into the reservoir was 0.224×10^9 , 1.57×10^9 , 3.24×10^9 , 36.95×10^9 and $727.15 \times 10^9 \mu\text{M}/\text{year}$, while outflow was 0.121×10^9 , 0.164×10^9 , 2.49×10^9 , 2.99×10^9 and $146.29 \times 10^9 \mu\text{M}/\text{year}$; therefore, nutrients retained in the reservoir were 0.103×10^9 , 1.406×10^9 , 0.75×10^9 , 33.96×10^9 , $580.86 \times 10^9 \mu\text{M}/\text{year}$, respectively. The presence of Nyumba Ya Mungu reservoir has interrupted nutrients' biogeochemistry and increased water retention time, which decreased nutrients' outflow from the reservoir. The increase in water residence time gives opportunity for biotic and chemical transformation of nutrients such as biological uptake and settling of particulate matter, which buries nutrients in sediment of the reservoir. Because of this property, Nyumba ya Mungu reservoir was considered as a nutrient sink. Retention of nutrients in the reservoir will have impacts to aquatic ecosystem, since measured surface and bottom DO were 7.82 and 0.78 mg/L. Increased retention of nutrients will prolong hypoxia, which will create unfavourable environment for most of the fishes and other organisms.

Effect of elevation and distance on nutrients' distribution

Figure 4 illustrates how nutrients' distribution varied in the main stream from above the reservoir to the river mouth. Various parameters behaved differently; this was caused by influence of tributaries, nutrients sinking, input of nutrients from mineral weathering and transformation of nutrients from one form to another. As stated earlier, Nyumba ya Mungu reservoir was a nutrient sink; therefore any increase in the nutrients' level downstream the reservoir was coming from other sources. Trend of increasing phosphate and DIP/DSi (Figure 4(d, h)) from Nyumba ya Mungu to the estuary in both seasons was caused by either input of phosphate from tributaries or input of phosphate from rock weathering. The basin has Proterozoic crystalline rocks downstream the reservoir and young igneous rock above the reservoir [48]. A study from Cook and McElhinny [49] has shown that phosphate is rich in old rocks relative to young one. Therefore, the presence of proterozoic rocks possibly have contributed to the elevated level of phosphate downstream. Further research is needed to

quantify contribution of phosphate from these rocks. Increasing DIP/DSi toward the estuary also showed that rate of increasing phosphate was higher than weathering of DSi. Besides, phosphate was from both anthropogenic input and rock weathering, whereas DSi was mainly from rock weathering and the presence of Proterozoic rocks led to low DSi.

Biological uptake and denitrification possibly played a role in decreasing DSi, nitrate, ammonium and urea downstream (Figure 4 a, b, c, and e). It was observed that denitrification and biological uptakes increase in shallow and low flowing rivers [50]. Most of the rivers in PRB were shallow with a low runoff average of 0.0014 mm/year, possibly led to a high rate of biological uptake and denitrification process. Furthermore, addition of DSi, nitrate, ammonium and urea from tributaries had no impacts on the main rivers. Significant positive correlation of nitrate with elevation ($r = 0.237$, $p \leq .05$) demonstrates decreasing of nitrate to the river mouth (Table 3). Decreasing DIN/DSi (Figure 4(i)) toward the estuary also revealed that biological uptake of nitrogenous compound and denitrification was higher than uptake of DSi, since the river was nitrogen-limiting for diatom growth.

Cluster analysis of sampled stations

Cluster analysis groups together stations according to their similarities. Based on concentration of nutrients, cluster analysis grouped stations into two main clusters (Figure 5). The bottom cluster had one station (12); this station had unique characteristics, including highest temperature, pH, Ammonium DSi and lowest DO. The cluster above is divided into two sub clusters with several groups for example group with stations (19,39,38) was dominated by stations from Kikuletwa tributaries, whereas group with stations (3,9,28) was dominated by tributaries from Mount Kilimanjaro.

Discussion

Concentration of nutrients in PRB compared with rivers from SWIO and other rivers over the world

The mean concentration of DSi was higher than other nutrients (Table 2); this was because concentration of DSi transported by rivers mainly depends on the amount of silicates present in the rocks and the hardness/softness of the rocks to weathering [51]. On a global scale there is increasing trend of DSi with decreasing latitude [52]; it was estimated that tropical rivers transfer about 7.68×10^{11} mol Si/yr compared to 4.5×10^{11} mol Si/yr from non-tropical rivers [53]. African

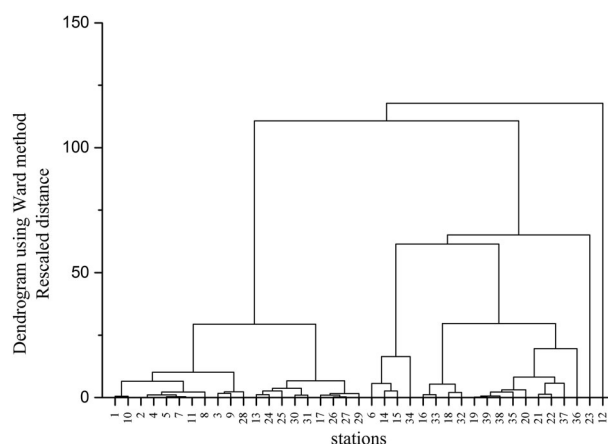


Figure 5. Cluster analysis of different stations represented by the same number as Table 1.

freshwaters have higher average DSi (about 389 μM) than any continent [54]. High concentration of DSi in Africa mostly caused by warm climate, which favour weathering and evaporation rate [51]. Since weathering of DSi increases with temperature and PRB is found in tropical region where temperature is always high, it is clear that PRB was expected to have a high content of DSi.

An interesting feature was that mean DSi in PRB was higher than not only average African freshwater rivers but also other tropical rivers, including Tana and Tapti (Table 2). This suggests that high level of DSi in PRB was not only caused by tropical weather illustrated by significant positive correlation between temperature and DSi ($r = 0.385$, $p \leq .01$) (Table 3). The presence of two volcanic mountains (Mount Kilimanjaro and Meru) played a role in the elevating level of DSi as it was observed in Japanese Archipelago [55] and other tropical volcanic Rivers of Barva, Poas and Arenal from Costa Rica [56].

Comparison with rivers from SWIO (Table 2) showed that average content of phosphate in the Sabaki River (4.27 μM) was higher than PRB (2.00 μM), whereas the opposite was the case for ammonium [29]. High phosphate was supported by intensive use of fertilizer in Kenya (52.5 kg/ha of arable land) relative to 4 kg/ha in Tanzania together with high growth domestic product (Table 4). Average ammonium and phosphate from Komati [30] and Thukela Rivers [31] in Swaziland and South Africa, respectively were higher than observed in PRB; the situation reflects high use of fertilizers in Swaziland and South Africa compared to that in Tanzania.

Observed seasonal nutrients' variability was contributed by seasonal change in natural and anthropogenic factors such as meteorological parameters (rainfall, temperature and evaporation), hydrology, damming and biogeochemical processes along the basin. Trend

Table 4. Factors regulating nutrients' yield in a River basin, Gross Domestic Product (GDP), amount of fertilizer per hectare of fertile land.

River name	Country	GDP (US Dollars)	Fertilizer (kg/ha)	Runoff (mm/year)
PRB	Tanzania	44,895	4.675	0.001
Sabaki	Kenya	63,398	52.541	0.004
Thukela	South Africa	312,798	57.718	0.015
Olifants	South Africa	312,798	57.718	485.830
Caura	Venezuela	515,700	179.848	2420.000
Ishikari	Japan	4123,258	256.664	1048.882
Penna	India	2073,543	157.522	0.013
Pra Basin	Ghana	37,864	35.824	0.035
Tapti	India	2,073,543	157.522	0.035
Trinity	USA	17,946,996	131,906	478.294
Tana	Kenya	63,398	52.541	0.004

Note: Fertilizers' use was adopted from [57].

GDP adopted from [58].

of increasing DSi and nitrite (Table 2) in the dry season was caused by the increase in temperature illustrated by significant positive correlation between temperature and DSi ($r = .45, p = .01$), together with increasing evaporation as observed in other tropical river such as Cachoeira River in Brazil [59]. Decreased DSi and nitrite in rainy season was caused by dilution factors contributed by rain water and a decrease in temperature. Increased nitrate, phosphate and urea in the wet season demonstrate uptake of those nutrients via rain runoff mostly from non-point sources to the rivers. Similar increase of nutrients in the wet season was observed in Weruweru catchment, Ruvi River and is common to SWIO Rivers [30,60,61].

Spatial and temporal nutrients variability was not statistically significant. Large standard deviation among stations shows that, there was great spatial variation of nutrients content caused by different levels of natural and anthropogenic activities which triggered different levels of nutrients in different stations. Different level of nutrients in different stations can also be seen in cluster analysis (Figure 5). Among 23 grouped stations, only one group contain 4 stations with similar characteristics, whereas other group contain few stations. Furthermore, various studies focusing on land-use and land cover change in different parts of the PRB have shown that forest cover declined, and cultivated land and human settlement have expanded differently in different areas [62].

Nutrients' yield from PRB to Indian Ocean, comparison with SWIO rivers and other global rivers

Nutrients' flux is a product of river discharge and nutrient content passing a given point in a given period of time, while nutrient yield is nutrient flux divide by

catchment area. Estimate of nutrient yield from PRB to the coast of Indian Ocean was done from station number 1 located on the river mouth. Concentration at this point was a result of both processes adding to and removal of nutrients from the river system [63]. Nutrients' yields of nitrite, phosphate, ammonium, nitrate and DSi were 2.6, 39.0, 45.2, 67.4 and 5444.8 mol/km²/yr¹, respectively. These yields were low to most of SWIO Rivers and other major rivers around the global having the same area as PRB area (Table 5). An interesting feature was that on the one hand, PRB had lower nutrients yield than Caura and Tana Rivers (Table 5), but on the other hand, average nutrients from PRB were higher than those two rivers (Table 2). Two factors played a role in reducing yield; these were low discharge and low use of fertilizers in the PRB (Tables 4 and 5). Discharge in PRB decreased with time, when we compare reported 26.8 m³/s average discharge in 2009 [22] with the current discharge of 15.1 m³/s; it is clear that within a short period, there was a significant decrease in discharge. Water abstraction for irrigation and hydroelectric power account for 90% of the available water (900 million m³); this is the major factor reducing river discharge [67]. Low discharge led to low runoff 0.0014 mm/year, whereas low runoff allow more time for biological uptake and denitrification process. Low use of fertilizer in Tanzania relative to other countries (Table 4) caused even the amount of nutrients taken up by flowing river to be low.

When we compared with large rivers from SWIO such as the Tana River, yield of nitrate, phosphate and DSi from PRB were 10%, 40% and 50% to that of Tana, while ammonium was almost within the same level (Table 5). Comparison with other large humid tropical rivers, yield of DSi in PRB was almost in the same order of magnitude as Zambezi River, 30% of Zaire River and 10% of Amazon River. DIN from PRB was about 20% of Zambezi, 5% of Zaire and 1% of Amazon [68].

Comparing yield from SWIO rivers with other rivers (Table 5), it was clear that yield from SWIO was lower than Asian Rivers (Ishikari, Tapti and Penna) and Trinity River from America. Asia and America have intensive use of fertilizers and high GDP relative to Africa (Table 4). Another reason was high discharge from Asian and American Rivers relative to SWIO Rivers led to high yield in Asian and American Rivers.

Possible impacts of nutrients to human and aquatic ecosystem around PRB

Average DIN/DIP in PRB was 20:1, while DSi/DIN was 13:1. These ratios were higher than Redfield ratio of 16:1 for phytoplankton [33] and 1:1 for diatoms growth [52],

Table 5. Comparison of nutrients' yield from PRB with other Rivers from SWIO and other major world rivers.

River	Country	Area (10 ³ km ²)	Yield in mol/km ² /yr (×10 ³)				SiO ₃ ²⁻	NO ₂ ⁻	DIN	Reference
			Discharge (m ³ /s)	NO ₃ ⁻	PO ₄ ³⁻	NH ₄ ⁺				
PRB	Tanzania	39.8	15.1	0.067	0.039	0.045	5.445	0.003	0.115	This study
Sabaki	Kenya	69.9	72.6		0.140	0.016				[29]
Thukela	South Africa	29.0	120.5	0.137	0.041	0.073		0.554		[31]
Olifants	South Africa	49.4			0.980					[64]
Caura	Venezuela	47.5		10.645	0.203	6.357				[32]
Ishikari	Japan	14.3	475.3	6709.677	96.774		25939.850			[33]
Penna	India	55.0	200.0		67736.840		1855.263		57142.86	[65]
Pra Basin	Ghana	23.0	221.8	242.857	354.839		10675.660			[66]
Tapti	India	61.0	598.9	1071.429	129.032		4151.645			[34]
Trinity	USA	46.0	697.2	1928.571	96.774		3078.430			[8]
Tana*	Kenya	120.0	126.8	0.590	0.095	0.040	10.164			[35]

respectively. High DIN:DIP suggests that Phosphorus was a limiting factor for phytoplankton growth, whereas high DSi:DIN showed that nitrogen was a limiting factor for diatom growth. High DSi/DIN indicates that PRB was conducive for diatoms' growth possibly the coast was dominated by diatoms which is a typical behaviour of tropical rivers enriched by DSi [33].

Concentration of ammonium in both seasons was below maximum level of 187.2 µM at pH 7 and 25°C for protection of aquatic organisms from ammonia toxicity [69]. Nitrate was above the maximum level of 210 µM for protection of aquatic ecosystem [70]. Similarly, phosphate was higher in most of the stations than recommend level of 0.5 µM at a point where the river enter lakes and 1.05 µM for rivers that do not discharge into the lakes/reservoirs [71]. Besides, high levels of nutrients to aquatic ecosystem health together with observed nutrients' retention capacity in Nyumba ya Mungu reservoir and hypoxia condition in Lake Jipe and Nyumba ya Mungu reservoir are threatening aquatic life. Therefore, fish harvest in Nyumba Ya Mungu reservoir and Lake Jipe decreased as fishermen claimed (2016, David Mjema, person commutation; unreferenced, see 'Notes'); the increase in nutrients content possibly was one of the reasons.

Measures need to be taken to reduce inflow of nutrients to Lake Jipe and Nyumba ya Mungu reservoir. On the other hand, content of nutrients in PRB were below Tanzania drinking water standards of 65 µM for nitrite, 111 µM for ammonium and 1210 µM for nitrate [72].

Conclusion

This study provides information on spatial and temporal dissolved nutrients' variability. There was both spatial and temporal nutrients' variability even though the variability was not statistically significant. Concentration of DSi was higher in the dry season than wet season, while the opposite was the case for nitrate, ammonium

and phosphate. Phosphate increased from upstream to river mouth, while DSi, ammonium, nitrite, urea and nitrate decreased from upstream to river mouth.

The basin was dominated by dissolved inorganic fraction of nitrogen and phosphorus in both seasons relative to organic fraction, signifying that inorganic fertilizers and wastes from industries were major cause of elevated concentration of nitrogen and phosphorus in the basin. Furthermore, weathering of rocks significantly elevates concentration of silicates.

In some stations, concentration of nutrients was higher than the recommended level for prosperity of aquatic ecosystem health. Observed hypoxia condition in Lake Jipe and Nyumba ya Mungu reservoir possibly was due to a high level of nutrients from agricultural activities and decomposition of organic matter. On the other hand, nitrite, nitrate and ammonium were lower than Tanzanian recommended level for drinking water standards.

Average concentrations of nitrate, phosphate and ammonium from PRB were in comparable level to rivers from SWIO and other rivers over the global, while concentration of DSi was higher than those rivers. Nevertheless, nutrient yield from PRB was lower than most of the rivers from SWIO as well as other rivers elsewhere.

Our research recommends the best farming practices such as contour farming, construction of wetland and efficient irrigation measures so as to reduce surface runoff. Reduced runoff will reduce uptake of nutrients from point and non-point sources to the rivers. Other measures to be considered are the best method for fertilizer application such as site-specific fertilizer application, which can help reduce uptake of nutrients from farmlands to the surface and groundwater. We also recommend frequent water quality monitoring to get reliable information for management measures so as to ensure that water in PRB meet standards level for both drinking and aquatic ecosystem health. Last but not least, we recommend future study on sampling and

measurement of nutrients in particulate phase so as to have a complete baseline nutrient data set covering both dissolved and particulate phase.

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